

# PATENT SPECIFICATION

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 JOHANNUS JACOBUS MULLER



## (54) PREPARATION OF SALTS OF CARBOXYMETHYLOXY-SUCCINIC ACID

- (71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—  
 The present invention relates to an improvement in the preparation of calcium carbonate and leaving a solution of Na-CMOS.  
 However, the calcium carbonate precipitate should be removed, and particularly in a continuous process for preparing CMOS builder salts this is a drawback.  
 The present invention now provides an improvement in the above process for preparing CMOS builder salts which is a drawback.

### ERRATUM

### SPECIFICATION NO 1379241

Page 1. Heading (72) Inventors for GABRIEL JACOBUS THEODORUS IANSBERGEN read GABRIEL JACOBUS THEODORUS IANSBERGEN

THE PATENT OFFICE  
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- between 11.3 and 12.5 at 25° C. Normally, the amount of zinc or alkaline earth metal cations used in the preparation of CMOS salts is from about 0.05 to 2.5 molar equivalents to each mole of maleic acid. These cations are generally added in the form of any convenient salt, oxide or hydroxide of zinc or alkaline earth metals. If a high pH is desired, alkaline materials, e.g. alkali metal hydroxides can be added additionally.  
 If minor amounts of zinc or alkaline earth metal cations are used in the above process it may be satisfactory to isolate the CMOS product by evaporation of the water from the reaction mass or to use the solution obtained directly in the production of, for example, detergent compositions. However, if the amount of zinc or alkaline earth metal cations used is higher, the cations in the CMOS product need to be changed for alkali metal, ammonium, or substituted ammonium cations. In the case of Ca-CMOS, this is conveniently done by the addition of sodium carbonate to the solution of the Ca-CMOS, thereby precipitating calcium carbonate and leaving a solution of Na-CMOS.  
 However, the calcium carbonate precipitate should be removed, and particularly in a continuous process for preparing CMOS builder salts this is a drawback.  
 The present invention now provides an improvement in the above process for preparing CMOS builder salts which is a drawback.  
 It has furthermore been found that still better results can be obtained if the solutions from which the precipitate is to be formed are stirred during the precipitation at a slow stirring rate. The latter greatly depends on the apparatus used, and is amongst other things governed by two major requirements, that is the stirring rate should be such that a minimum amount of air is incorporated in the solution and agglomerates of precipitated particles should not be significantly destroyed.  
 The present invention therefore also provides an improvement in the production of CMOS detergency builder salts from salts of maleic and glycolic acid in the presence of zinc or alkaline earth metal cations, in which the improvement comprises adding a suitable alkali metal, ammonium or substituted ammonium carbonate to the CMOS reaction product solution maintained at a temperature of between 70° C and 100° C, to form a pre-

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## (54) PREPARATION OF SALTS OF CARBOXYMETHYLOXY-SUCCINIC ACID

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improvement in the process for preparing water-soluble salts of carboxymethyloxysuccinic acid, which hereafter will be referred to as CMOS.

Water-soluble alkali metal, ammonium, and substituted ammonium salts of CMOS have been proposed as phosphorus-free detergency builders. These CMOS detergency builder salts are preferably prepared by reacting salts of maleic acid and glycolic acid in an aqueous alkaline medium containing zinc or alkaline earth metal cations. The pH of the medium should be at least 8 and preferably lie between 11.3 and 12.5 at 25° C. Normally, the amount of zinc or alkaline earth metal cations used in the preparation of CMOS salts is from about 0.05 to 2.5 molar equivalents to each mole of maleic acid. These cations are generally added in the form of any convenient salt, oxide or hydroxide of zinc or alkaline earth metals. If a high pH is desired, alkaline materials, e.g. alkali metal hydroxides can be added additionally.

If minor amounts of zinc or alkaline earth metal cations are used in the above process it may be satisfactory to isolate the CMOS product by evaporation of the water from the reaction mass or to use the solution obtained directly in the production of, for example, detergent compositions. However, if the amount of zinc or alkaline earth metal cations used is higher, the cations in the CMOS product need to be changed for alkali metal, ammonium, or substituted ammonium cations. In the case of Ca-CMOS, this is conveniently done by the addition of sodium carbonate to the solution of the Ca-CMOS, thereby precipitating

calcium carbonate and leaving a solution of Na-CMOS.

However, the calcium carbonate precipitate should be removed, and particularly in a continuous process for preparing CMOS builder salts this is a drawback.

The present invention now provides an improvement in the above process for preparing CMOS builder salts, which improvement comprises forming a precipitate of the zinc or alkaline earth metal carbonate in the CMOS reaction product solution, by first adjusting the precipitation temperature of the CMOS reaction product solution to between 70° C and 100° C, then adding an alkali metal, ammonium or substituted ammonium carbonate, and finally filtering off the precipitate thus formed.

It was found that with increasing precipitation temperatures the subsequent filtration was significantly more efficient. In general the precipitation temperature should lie between 70° C and 100° C, and preferably between 70° C and 90° C.

It has furthermore been found that still better results can be obtained if the solutions from which the precipitate is to be formed are stirred during the precipitation at a slow stirring rate. The latter greatly depends on the apparatus used, and is amongst other things governed by two major requirements, that is the stirring rate should be such that a minimum amount of air is incorporated in the solution and agglomerates of precipitated particles should not be significantly destroyed.

The present invention therefore also provides an improvement in the production of CMOS detergency builder salts from salts of maleic and glycolic acid in the presence of zinc or alkaline earth metal cations, in which the improvement comprises adding a suitable alkali metal, ammonium or substituted ammonium carbonate to the CMOS reaction product solution maintained at a temperature of between 70° C and 100° C, to form a pre-

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precipitate the zinc or alkaline earth metal carbonate under stirring at such a rate, that no significant amount of air is incorporated in the solution and that agglomerates of precipitated particles are not significantly destroyed, and filtering off the precipitate thus formed.

The alkaline earth metal cations generally used in the above process are calcium, magnesium, strontium and barium cations. Preferably calcium cations are used, e.g. as hydroxide or carbonate. The precipitation of the latter from the Ca-CMOS solution is conveniently done by adding sodium carbonate thereto.

The molar ratio of glycolic acid to maleic acid in the reaction is normally from about 1:2 to about 2:1, preferably from 1.05:1 to about 1.2:1, and the total concentration of glycolic and maleic acid is normally from 0.5 to 5.0 molal., preferably from 2 to 3.5 molal. The temperature at which the reaction is carried out is normally from 40 to 200° C, preferably from about 60 to 130° C, (at higher temperatures the reaction needs to be done under pressure). The precipitation temperature, if need be, is adjusted by appropriate heating or cooling, depending upon the reaction temperature.

The invention will now be illustrated by way of example.

#### EXAMPLE.

Maleic anhydride (0.3 mole) was suspended in water (150 ml) at room temperature and stirred for 10—15 minutes to obtain a solution of maleic acid. Glycolic acid (0.33 moles) was then added and dissolved under stirring. Calcium hydroxide (about 0.54 mole), sufficient to attain a pH of 12.0, was next added while stirring the reaction mixture vigorously. The mixture was heated to reflux temperature and maintained at reflux temperature (100° C) for 30 minutes while stirring vigorously.

With 8 of the Ca-CMOS-solutions obtained as above, filtration experiments were carried out, whereby the precipitation temperature, the reaction pH and the rate of stirring were varied. The precipitation in each of the experiments was effected by adding finely ground technical sodium carbonate (about 0.56 mole), and then stirring the resulting slurry for fifteen minutes.

The times needed to obtain 50 ml and 100 ml of filtrate (total filtrate about 150 ml) were recorded. The results are summarized in the table below:

Experiment No.	Precipitation temp. (°C)	pH	Stirring rate (rpm)	Time (min.) to obtain	
				50 ml. filtrate	100 ml. filtrate
1	40	reaction pH	300	17.5	42.0
2	80	„	„	5.0	16.5
3	40	8.0	„	4.0	16.0
4	80	8.0	„	2.1	7.2
5	40	reaction pH	40	19.0	34.0
6	80	„	„	1.0	3.3
7	40	8.0	„	1.5	4.0
8	80	8.0	„	0.8	2.6

Where the pH is given as 8.0, it was attained by addition of hydrochloric acid before sodium carbonate addition.

From these experiments it is clear that at higher precipitation temperatures the filtration time significantly decreases, and that at lower stirring rates even better results are obtained. Under optimum conditions of stirring and precipitation temperatures the effect of changing the pH of the Ca-CMOS-solution on the

filterability of the calcium carbonate produced appears to be small. The calcium ion levels of a dried sample of the filtrates were shown to be about 0.3 wt%. On storage for weeks at room temperatures the filtrates remained clear.

Attention is directed to our U.K. Patent Specification No. 1,327,115 which describes and claims carboxymethyloxysuccinic acid and its salts, together with processes for their pro-

duction and also the use of the salts as detergency builders.

WHAT WE CLAIM IS:—

1. A process for the preparation of a solution of water-soluble alkali metal, ammonium or substituted ammonium carboxymethyloxysuccinate salts by reacting salts of maleic and glycolic acid in an aqueous medium of pH at least 8 in the presence of zinc or alkaline earth metal ions at a temperature between 40 and 200° C, adjusting the precipitation temperature to between 70° C and 100° C, then adding an alkali metal, ammonium or substituted ammonium carbonate and finally filtering off the precipitate of the zinc or alkaline earth metal carbonate then formed.

2. A process according to Claim 1, in which the precipitation temperature is adjusted to between 70 and 90° C.

3. A process according to Claim 1 or 2, in which the solution is stirred during precipitation. 20

4. A process according to claim 1 substantially as hereinbefore described with reference to the example. 25

5. A solution of an alkali metal, ammonium or substituted ammonium carboxymethyloxysuccinate salt whenever produced by a process according to any of the preceding Claims. 25

6. An alkali metal, ammonium or substituted ammonium carboxymethyloxysuccinate salt produced by drying a solution according to Claim 5. 30

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